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Relaxation dynamics of excited states of Er³⁺ in YVO₄ single crystals

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ABSTRACT

Crystals of Er:YVO₄ were grown by Czochralski method. Uniformly doped and good quality crystals have been obtained. The lifetimes of the ⁴S_{3/2}, and the luminescence dynamics were studied as a function of temperature in the region 5–500K. The green luminescence around 550 nm has been observed in excitation by the Ti:sapphire laser into ⁴I_{11/2} level. The excitation spectrum recorded for ⁴S_{3/2} has been compared with absorption cross section spectrum and calculated ESA spectrum for ⁴I_{11/2}–⁴F_{7/2} transition. The contribution of ESA process in upconversion phenomenon under excitation into ⁴I_{11/2} has been assessed. The emission cross-section and the gain coefficient for ⁴I_{13/2}–⁴I_{15/2} transition of Er³⁺ in YVO₄ have been calculated.

Keywords: Er:YVO₄ crystals, absorption spectrum, green luminescence, doping.

1. INTRODUCTION

In the last few years Er³⁺ doped YVO₄ has been considered as a potential laser material in the IR spectral region ¹. However, that real potential strongly depends on the relaxation dynamics of excited states to lower states and upconversion processes. For Er:YVO₄ the ESA and SE cross-section spectra for ⁴I_{13/2}–⁴I_{15/2} the transition do not overlap ². Accordingly, losses of radiation by ESA at potential laser transition should be negligible but no laser emission of Er³⁺:YVO₄ has been observed yet. The absorption spectra, emission spectra and fluorescence dynamics of Er³⁺:YVO₄ have been reported³. Upconverted green luminescence has been observed by excitation into ⁴F_{9/2}, ⁴I_{9/2}, and ⁴I_{11/2} ¹. The absorption cross-section (σ_{ESA}) from ⁴I_{13/2} level of Er:YVO₄ have been determined experimentally ³. In this study, the temperature dependence of ⁴S_{3/2} decay in the range 5–500K was investigated and compared with predictions of multiphonon relaxation model. The contribution of ESA process to the upconversion phenomenon under excitation into ⁴I_{11/2} was considered. The emission cross-section and the gain coefficient for ⁴I_{13/2}–⁴I_{15/2} transition of Er³⁺ in YVO₄ were calculated.

2. EXPERIMENTAL

Crystals of Er:YVO₄ were grown by Czochralski method. Uniformly doped and good quality crystals have been obtained. The concentration of Er³⁺ in the crystals studied was 0.5, 2, and 4 at %. Absorption spectra were measured with a Varian model 2300 absorption spectrophotometer. The sample luminescence was excited by a Ti:sapphire laser emitting at 970 nm or by Continuum OPO model Surelite I pumped by third harmonic of Nd:YAG laser and dispersed by 1m double grating monochromator, detected by photomultiplier or InSb detector and analysed by a Stanford Model SRS 250 Boxcar integrator. In luminescence decay measurements a digital oscilloscope Tektronix model TDS 3052 has been used. For low temperature measurements, the samples were mounted in Oxford Model CF 1204 continuous flow liquid helium cryostat equipped with a temperature controller.

3. RESULTS AND DISCUSSION

Room temperature absorption spectrum of Er³⁺ ions on YVO₄ is shown in Fig.1. The observed absorption lines are not fully resolved and inhomogeneously broadened.

The temperature dependence of luminescence lifetime of the $^4S_{3/2}$ level of Er^{3+} in YVO_4 for samples containing 0.5 at % and 4 at % of erbium is shown by solid circles and squares respectively in Fig.2. The samples were excited by OPO at 523 nm into the level $^2\text{H}_{11/2}$. The obtained data are consistent with data presented previously for room temperature and at 77K ^{3,4}. In the phenomenological approach of Riseberg and Moos ⁵ the expected temperature dependence of $^4S_{3/2}$ lifetime has been drawn according to the formula:

$$\tau = \frac{12A_r(^2\text{H}_{11/2}) \exp\left(-\frac{\Delta E}{kT}\right) + 4A_r(^4S_{3/2})}{12 \exp\left(-\frac{\Delta E}{kT}\right) + 4} + A_0 \left(\frac{\exp \frac{\hbar\omega}{kT}}{\exp \frac{\hbar\omega}{kT} - 1} \right)^p \quad (1)$$

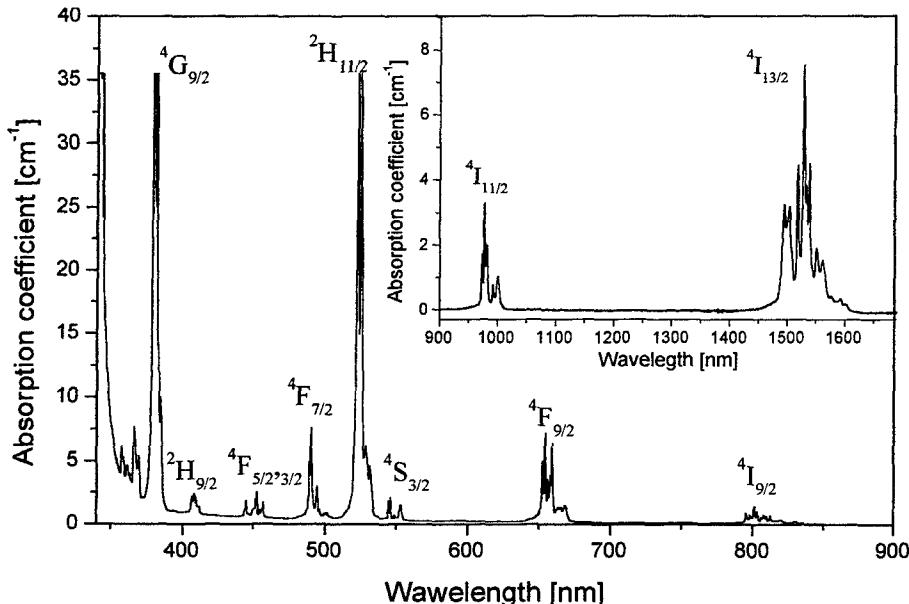


Fig. 1 Absorption spectrum of Er^{3+} ions in YVO_4 crystal recorded at room temperature.

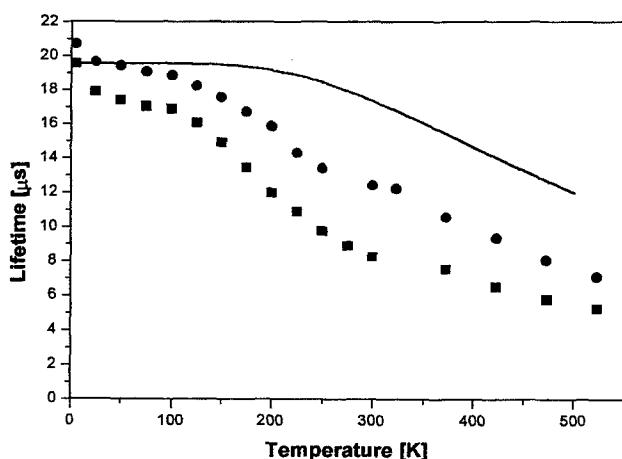


Fig. 2 Temperature dependence of luminescence lifetime of the $^4S_{3/2}$ level of Er^{3+} in YVO_4 crystal. Data indicated by solid circles and squares for samples containing 0.5 at % and 4 at % of erbium, respectively. See text for the explanation of theoretical line.

where: $A_r(^2\text{H}_{11/2})$, $A_r(^4S_{3/2})$ denote the values of the radiative transition rates as given in ⁴, $\Delta E=709 \text{ cm}^{-1}$ is the energy gap between $^2\text{H}_{11/2}$ and $^4S_{3/2}$ levels. A_0 denotes the spontaneous multiphonon transition rate, $\hbar\omega=890 \text{ cm}^{-1}$ is the phonon energy ⁶ and $p=4$ is the number of phonons needed to cover the energy gap between $^4S_{3/2}$ and $^4F_{9/2}$ levels. A_0 has been calculated from the inverse of luminescence lifetime measured and 5K. The solid line in Fig.2 presents the theoretical approach derived from equation (1). It cannot predict the experimental temperature dependence of lifetime for the $^4S_{3/2}$ level because the experimentally determined lifetime decreases quickly with increasing temperature. The reason of

observed discrepancy is not clear yet. This may be caused by interaction of active ions with structural defects.

To elucidate a mechanism of upconversion the excitation spectrum of $^4S_{3/2}$ luminescence was recorded at room temperature. The sample was excited by tuneable Ti:sapphire laser in the range 968-988 nm and detected at 552.5nm. The resulting excitation spectrum is presented in Fig.3 by solid line with the σ_{GSA} spectrum (dotted line) in the same wavelength domain. From the analysis of the energy level diagram of Er^{3+} in YVO_4 presented in ³, we have built the σ_{ESA} spectra corresponding to $^4I_{11/2}-^4F_{7/2}$ transition after pumping around 970 nm using the expression ⁷.

$$\sigma_{ESA}^{J \rightarrow J'}(\lambda) = \tilde{\lambda} S_{calc} (J - J') \sum_{i,j} \frac{f_i}{2J+1} \frac{1}{\pi} \frac{\Delta\lambda/2}{(\lambda - \lambda_{ij})^2 + (\Delta\lambda/2)^2} \quad (2)$$

where : f_i is the Boltzmann factor for i-th crystal field level of the starting multiplet J of ESA transition. This factor has been approximated by $1/(2J+1)$; λ_{ij} are the expected wavelength position of ESA lines. In order to calculate λ_{ij} , the experimentally observed crystal-field energy levels of Er^{3+} ion in YVO_4 , for the ${}^4\text{I}_{11/2}$ and ${}^4\text{F}_{7/2}$ were taken from Table 3 in³. $\Delta\lambda$ is the linewidth of ESA line assumed to has a Lorentzian profile and the same as of GSA line around 970 nm i.e. $\Delta\lambda=1\text{nm}$; $\tilde{\lambda}$ is the average wavelength of the transition $\tilde{\lambda}=9.74 \times 10^{-5} \text{cm}$. S_{calc} has been calculated by using expression:

$$S_{calc} = C(n) S({}^4\text{I}_{11/2} - J) \quad (3)$$

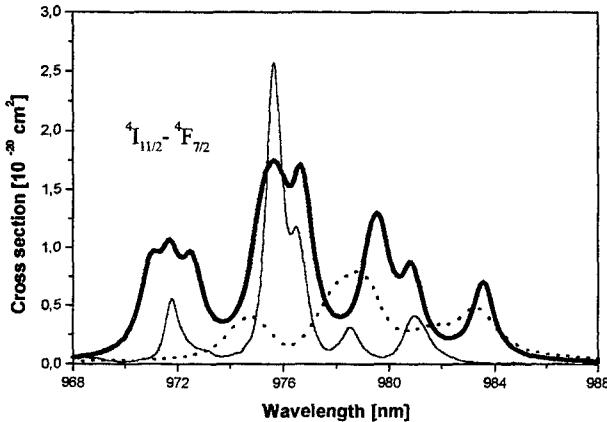


Fig. 3 Room temperature excitation spectrum of ${}^4\text{S}_{3/2}$ luminescence of Er^{3+} in YVO_4 – solid line with σ_{GSA} spectrum for ${}^4\text{I}_{15/2}-{}^4\text{I}_{13/2}$ (dotted line). For the comparison, the calculated spectrum for $\sigma_{ESA} {}^4\text{I}_{11/2}-{}^4\text{F}_{7/2}$ transition is presented - bold line.

$$\text{where: } C(n) = \frac{(n^2 + 2)^2}{9n} \frac{2\pi^3 e^2}{3hc} \quad (4)$$

$$\text{and } S({}^4\text{I}_{11/2} - J) = \sum_{i=2,4,6} \Omega_i \left| \langle {}^4\text{I}_{11/2} | U^{(i)} | J \rangle \right|^2 \quad (5)$$

S is the electric – dipole transition strength, $U^{(i)}$ are matrix elements and Ω_i are Judd-Ofelt parameters. S_{calc} was calculated taking to account Ω_i parameters from³, $S_{calc}=0.893$ and $C(n)=0.0283$ for YVO_4 ($n=2.02$). In this calculation it is assumed that all transitions between the Stark components have the same intensity and the same polarisation.

The resulting spectrum is presented in Fig.3 by bold line. It can be seen that the excitation spectrum coincides with both the ESA transition and GSA transition lines. The overlap with the σ_{GSA} is weaker than with σ_{ESA} . Thus, we conclude that the losses by ESA from ${}^4\text{I}_{11/2}$ when exciting at 970nm may be appreciable. It was reported⁸ that in Er^{3+} doped fluorozirconate glasses, ESA processes were the principal processes for the upconversion emission near 550nm.

To determine the emission cross section for ${}^4\text{I}_{13/2}-{}^4\text{I}_{15/2}$ transition of Er^{3+} in YVO_4 we have used the reciprocity method⁹. This method is based on the relation between absorption cross section $\sigma_a(\lambda)$ and emission cross section $\sigma_{em}(\lambda)$ by the following relation

$$\sigma_{em}(\lambda) = \frac{Z_{low}}{Z_{up}} \sigma_a(\lambda) \exp\left(\frac{Z_{up} - E(\lambda)}{k_B T}\right) \quad (6)$$

where: Z_{low} , Z_{up} are the partition functions of lower and upper level, respectively, defined as

$$Z_{low} = \sum_{i=1}^n g_i \exp\left(\frac{-E_i}{k_B T}\right) Z_{up} = \sum_{j=1}^m g_j \exp\left(\frac{-(E_j - E(\lambda))}{k_B T}\right)$$

where: $g_i(g_j)$ is a degeneration of sublevel, $E_i(E_j)$ is the energy of the sublevel, E_{ZL} is an energy separation between the lowest crystal field components of the upper and lower multiplets, and k_B is the Boltzmann constant. The ratio Z_{low}/Z_{up} calculated using the above values is equal to 1.06. The energies of E_i and E_j Stark sublevels for ${}^4\text{I}_{15/2}$ and ${}^4\text{I}_{13/2}$ were taken from Table 3 in³. Calculated

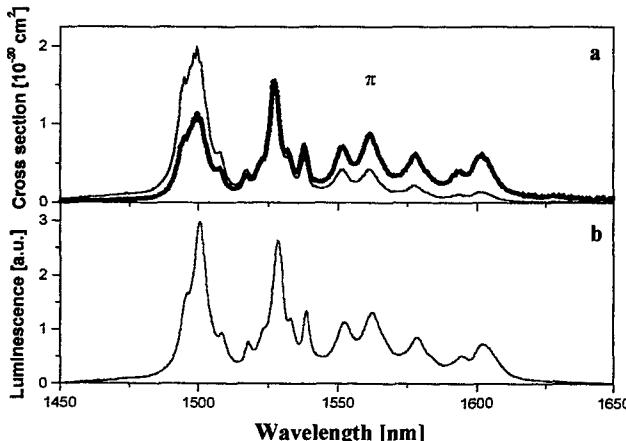


Fig. 4 a) absorption cross section (solid line) and calculated spectra and emission cross section (bold line) b) luminescence spectra recorded for ${}^4\text{I}_{13/2}-{}^4\text{I}_{15/2}$ under excitation by Ti:sapphire laser emitting at 970 nm. All spectra for π polarisation

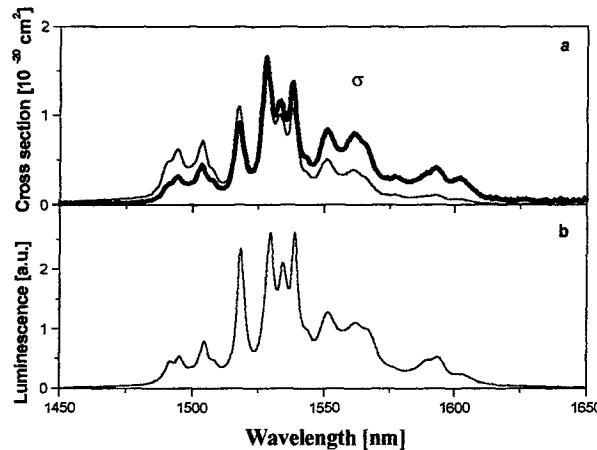


Fig. 5 a) absorption cross section (solid line) and calculated spectra and emission cross section (bold line) b) luminescence spectra recorded for ${}^4\text{I}_{13/2} - {}^4\text{I}_{15/2}$ under excitation by Ti:sapphire laser emitting at 970 nm. All spectra for σ polarisation

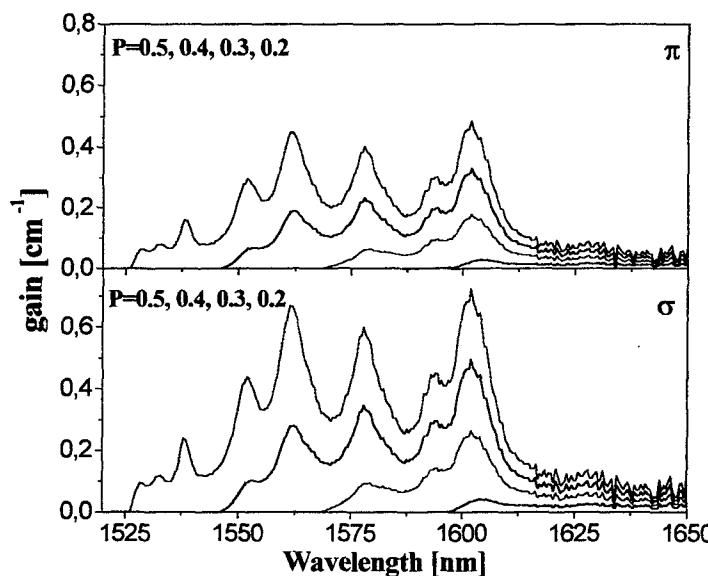


Fig. 6 Gain coefficient calculated for several reasonable values of P for ${}^4\text{I}_{13/2} - {}^4\text{I}_{15/2}$ transition Er^{3+} in YVO_4

cross section $\sigma_{\text{em}}(\lambda)$ for π and σ polarisation is indicated by bold lines in Fig. 4a and Fig. 5a, respectively. Corresponding $\sigma_a(\lambda)$ spectra are also given by solid lines in those figures. The luminescence spectra for π and σ polarisation recorded under excitation by Ti:sapphire laser emitting at 970 nm are presented in Fig. 4b and Fig. 5b. It can be seen that spectra derived by reciprocity method are in a good agreement with luminescence spectra recorded for both π and σ polarisation. From the estimated $\sigma_a(\lambda)$ and $\sigma_{\text{em}}(\lambda)$ the gain coefficient $G(\lambda)$ was calculated using formula¹⁰:

$$G(\lambda) = N [P\sigma_{\text{em}}(\lambda) - (1-P)\sigma_a(\lambda)] \quad (7)$$

where N is the Er^{3+} concentration, P is a population inversion parameter defined as a density of ions in upper state divided by N . Results of calculation for several reasonable values of P are shown in Fig. 6. The presented results are consistent with that presented by F.S. Ermeneux et al.¹ and suggest the possible application of $\text{Er}: \text{YVO}_4$ as a laser material operating near $1.6\mu\text{m}$.

4. CONCLUSION

The theoretical approach basis on multiphonon relaxation model cannot predict the experimental temperature dependence of lifetime for the ${}^4\text{S}_{3/2}$ level. The participation of the ESA process from ${}^4\text{I}_{13/2}$ in upconverted green phenomenon under excitation at 970 nm is appreciable. The emission cross section spectra derived by reciprocity method are consistent with recorded luminescence spectra of ${}^4\text{I}_{13/2} - {}^4\text{I}_{15/2}$ transition for both π and σ polarisation. The positive gain coefficient for ${}^4\text{I}_{13/2} - {}^4\text{I}_{15/2}$ transition suggest the possible application of $\text{Er}: \text{YVO}_4$ as a laser material operating near $1.6\mu\text{m}$.

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